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Activation of Nitrogen by Alkali Metal-Promoted Transition Metal

III. On the Adsorption of Nitrogen Over the Alkali Metal-Promoted Ruthenium Catalyst

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The characteristics of adsorption of both nitrogen and hydrogen by alkali metal-promoted ruthenium on active carbon (AC) were studied at temperatures from 200 to 300°C and reduced pressures. Extensive nitrogen adsorption takes place on Ru-K and Ru-AC-K, but not on Ru-AC or K-AC. It is suggested that N_2 is first chemisorbed on Ru and migrates to alkali metal. The alkali metal seems to be partly transformed into amide under the synthesis condition, giving rise to a delayed appearance of ammonia in gas phase.

INTRODUCTION

It has been reported that the catalytic activity of transition metals for ammonia synthesis is remarkably promoted by addition of alkali metal (*1*). The promoter action is likely to be provided by a charge transfer from alkali metal to transition metal which facilitates the formation of anionic intermediate over the transition metal (*2*, *3*). On the other hand, it has been found that a large amount of nitrogen and/or hydrogen is sorbed by the ruthenium-active carbon-potassium catalyst on introduction of synthesis gas at 200–400°C (*3*), whereas the location of sorbed nitrogen has not been clear. The present paper deals with the adsorption of nitrogen of Ru-AC-K catalyst in the absence or presence of hydrogen, and discusses the nature of nitrogen sorption along with the mechanism of ammonia synthesis.

EXPERIMENTAL METHODS

Catalyst Preparation

The catalysts used here were mostly composed of ruthenium, active carbon (AC) and potassium (or sodium). The method of catalyst preparation was the same as that reported previously (*3*). When azide of potassium or sodium was used instead of alkali metal, it was added in the following manner. The hydrogen-reduced Ru-AC or the AC without Ru was mixed mechanically with KN_3 (or NaN_3) powder in the reaction tube, evacuated at 150°C, heated up to 280–320°C to decompose KN_3 (or NaN_3) for 20 hr and then heated to 400°C for 20 hr. The compositions and the activities of all the catalysts used in this study are listed in Table 1.

Measurement of Gas Adsorption and Ammonia Synthesis Rate

The apparatus and procedure for the measurement of ammonia synthesis rate were the same as was reported previously. Measurement of gas adsorption was carried out *in situ*. N_2 and H_2 content of the gas mixture was analyzed by gas chromatography. The determination of ammonia formed and trapped was intermittently made by evaporating it.

RESULTS AND DISCUSSION

Interaction of N_2 with Ru-AC-K Catalyst

The time courses of nitrogen uptake on Ru-AC-K at 260–280°C are shown in

TABLE 1
PROPERTIES OF RUTHENIUM CATALYSTS

Catalyst no.	Support	Ru wt%[a]	Catalyst wt (g)[b]	Alkali metal	Alkali metal wt%[c]	NH_3 synth. rate at 250°C (ml/hr/g-cat)[d]
1	Glass	3.85	11.0	K	1.73	0.10
2	AC[e]	2.5	2.5	Na	—	0.33
3	AC	5.0	3.0	K	16.9	—
4	AC	5.0	2.5	K	20.6	7.0
5	AC	10.0	2.5	K	12.3	—
6	AC	10.0	2.5	K	12.1	5.4
7	AC	5.0	2.5	K	7.3	2.2
8	AC	5.0	2.5	K	13.7	2.8
9	AC	5.0	2.5	K	7.4	1.3
10	AC	5.0	2.5	K	9.2	3.3
11	AC*[f]	5.0	2.5	K	18.4	5.0
12	AC*	5.0	2.5	K	27.6	—
13	AC*	5.0	2.5	K	19.7	8.6
14	AC	0	1.0	—	0.0	—
15	AC	2.5	1.0	—	0	—
16	AC	0	2.5	K	4.4	—
17	AC	5.0	2.5	NaN_3	10.1	0.21
18	AC	0	1.25	NaN_3	10.1	—
19	AC	4.9	1.0	KN_3	18.4	1.8
20	AC	2.8	1.0	KN_3	21.1	0.80

[a] % for support wt.

[b] Weight of ($RuCl_3 \cdot 3H_2O$ + support) before reduction.

[c] Wt% for catalyst before reduction.

[d] Reaction condition; $N_2 + 3H_2 = 600$ Torr, flow rate 4.5 STP liters/hr.

[e] Coconut active carbon.

[f] Tsurumi coal.

TABLE 2
NITROGEN UPTAKE[a] BY Ru–AC–K CATALYST

Catalyst no.	Ru (mg-atom/g-cat)	K (mg-atom/g-cat)	N uptake (mg-atom/g-cat)	Temp (°C)
1	0.35	0.42	0.01	295
10	0.44	2.4	0.16	250
8	0.44	3.5	0.16	275
6	0.78	3.1	0.30	262
4	0.44	5.3	0.38	235
11	0.44	4.7	0.46	250
3	0.44	4.3	0.48	300
12	0.44	7.1	0.60	260

[a] Nitrogen pressure; 300 Torr except for No. 3 (540 Torr).

Fig. 1. The nitrogen uptake attains saturation within a few hours. The saturated nitrogen uptakes by Ru–AC–K catalysts of different contents of Ru and K, determined at 300 Torr (1 Torr = 133.3 N m^{-2}) and 235 to 300°C, are listed in Table 2, where it is conceivable that the nitrogen uptake depends upon K content rather than Ru content. Although the adsorption temperature is different, the effect of temperature is not extensive as observed in Nos. 3 and 11 where K content is similar but the temperature is different by 50°C. Figure 2 shows that the nitrogen uptake increases with K content. On the other hand, the nitrogen uptakes on AC (No. 14 in Table 1), 2.5% Ru–AC (No. 15) and 4.4% K–AC (No. 16) were as small as 0.01–0.02 mg-atom/g-cat. Accordingly, the

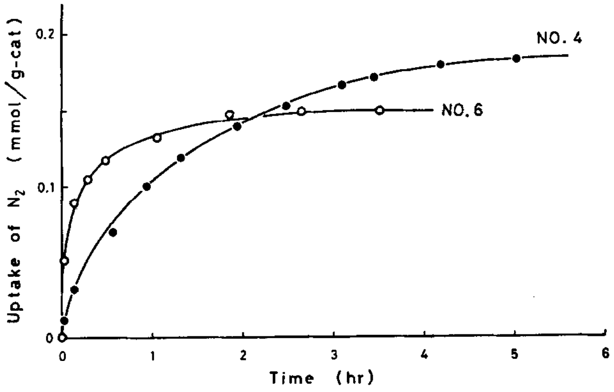

FIG. 1. Time course of N_2 uptake by Ru–AC–K under 300 Torr, 262°C (catalyst No. 6 in Table 1) and 281°C (catalyst No. 4).

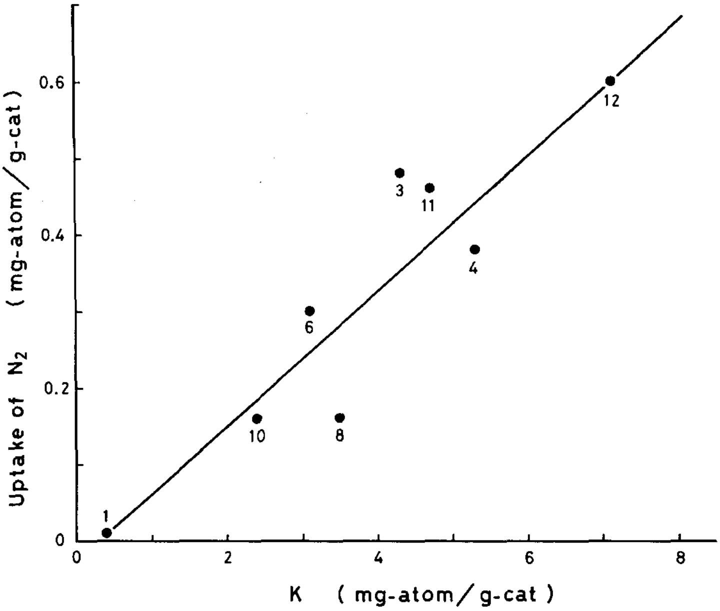

FIG. 2. Dependence of N_2 uptake on K added (from Table 2).

observed nitrogen uptake should be ascribed to the combination of Ru and K. Note in Table 2 that the number of nitrogen atoms taken up by the Ru–AC–K can exceed that of Ru in the catalyst. This fact suggests that nitrogen is first dissociated into atoms over ruthenium and then migrates on to potassium surface where it is accumulated. Known nitrogen compounds of alkali metal are nitride and azide. Nitrides of Na and K are thermally unstable. That is, Na_3N and K_3N reportedly decompose at 150°C and lower temperature, respectively (*4*). Azides are known to be relatively stable. The decomposition temperatures are reportedly 300°C (NaN_3) and 350°C (KN_3) (*4*). However, the mixture of azide and AC or Ru–AC (Nos. 17–

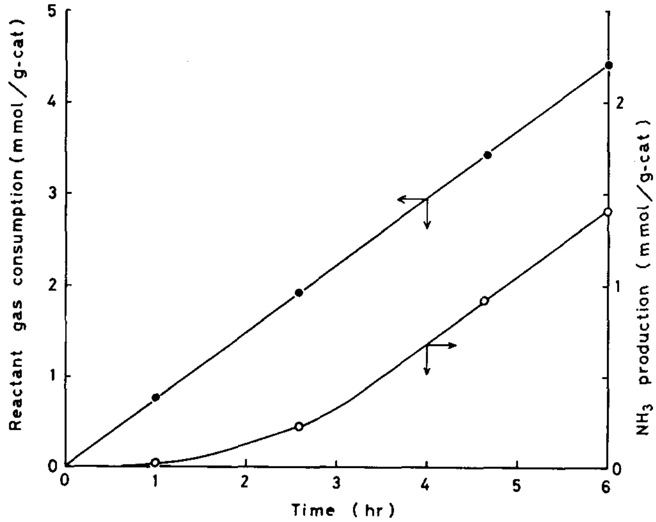

FIG. 3. Time course of gas consumption and NH_3 production by catalyst No. 13 at 257°C ($N_2 + 3H_2$ = 600 Torr).

TABLE 3

Initial Uptake of $N_2 + H_2$ Under the Synthesis Condition[a]

Catalyst no.	Ru (mg-atom/g-cat)	K (mg-atom/g-cat)	Uptake of $N_2 + H_2$ (mmol/g-cat)
7	0.44	1.9	0.06
9	0.44	1.9	0.13
6	0.78	3.1	0.48
13	0.44	5.0	1.6

[a] $N_2 + 3H_2$ = 600 Torr, Temp = 262 ± 6°C.

20) was found to decompose slowly even at 250°C and the decomposition was complete at 300 ± 20°C in 20 hr. The decomposition product was identified to be molecular nitrogen. Soon after the complete decomposition of azide (KN_3, NaN_3) mixed with Ru–AC, the Ru–AC catalyst began to take up nitrogen and acquired the catalytic activity for the ammonia synthesis as shown in Table 1. This result can be understood as the activation by potassium metal, the decomposition product. Thus azide or nitride is unlikely to be formed by the interaction of alkali metal with nitrogen. Probably the nitrogen atoms migrated from Ru surface remain on the potassium surface, without forming bulk compound. Note that all the adsorbed nitrogen including that on potassium is displaced with gas phase nitrogen as revealed by the ^{15}N tracer experiment (*5*).

Interaction of Reactant Gas ($N_2 + 3H_2$) with Ru–AC–K Catalyst

On introduction of reactant gas (N_2 + $3H_2$) over Ru–AC–K, gas uptake only was observed at first without production of ammonia. Figure 3 shows the time course of uptake and ammonia production by catalyst No. 13 at 257°C. In this case, a steady rate of ammonia production was attained after 4 hr, when the rate of gas uptake was equal to the rate of ammonia production. The apparent induction period is thus estimated to be 2 hr. During this period, 1.6 mmol/g-cat of reactant gas was absorbed. Such initial uptakes were measured over catalysts of different composition at around 260°C and shown in Table 3. The initial uptake tends to increase with the potassium content.

Hydrogen uptake was separately measured on Ru–AC, K–AC and AC at 315°C and 300 Torr. The amounts of hydrogen uptake after 1 hr were 0.22 mg-atom/g-cat on 2.5% Ru–AC (No. 15), 0.24 mg-atom/g-cat on 4.4% K–AC (No. 16) and negligibly small on AC. Since the hydrogen uptake by Ru–AC and K–AC was not negligible, the

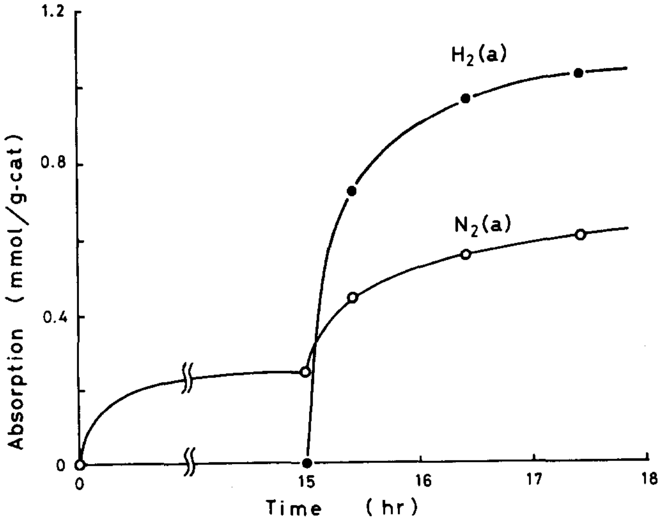

Fig. 4. Time course of N_2 and H_2 uptake on No. 3 at 300°C (N_2 = 540 Torr till 15 hr, $N_2 + 3H_2$ = 600 Torr after 15 hr).

uptake of synthesis gas shown above must be the sum of uptakes of nitrogen and hydrogen.

Thus the synthesis gas uptake was examined by gas phase analysis. After nitrogen was adsorbed on Ru–AC–K (No. 3) at 300°C and 540 Torr for 15 hr, the gas phase nitrogen was replaced by synthesis gas ($N_2 + 3H_2 = 600$ Torr) and the change of gas phase composition was followed by gas chromatography. The results are illustrated on Fig. 4. It is seen that both uptakes of nitrogen and hydrogen rapidly increase on introduction of the synthesis gas and later slowly increase. The increase in nitrogen uptake must be caused by the presence of hydrogen, which indicates that some N–H compound is formed. In this respect it is to be noted that the ratio of incremental uptake of hydrogen to nitrogen may be assessed as 2 in later slow uptake. This result would be a sign of NH_2 formation. Since the synthesis gas uptake tends to increase with the amount of potassium added as shown in Table 3, the NH_2 formed seems to lie on potassium. Indeed, potassium is known to react with ammonia forming amide, which is stable at 250–300°C. Thus it would be natural to assume that the potassium on Ru–AC–K catalyst is partly transformed into amide during ammonia synthesis. The apparent induction period shown in Fig. 3 may be accounted for by the reaction between the initially produced ammonia and potassium to form amide. Since both nitrogen and hydrogen uptakes are much less than potassium on atom basis ($N/K = 0.14$, $H/K = 0.24$), added potassium should be largely metallic.

REFERENCES

1. OZAKI, A., AIKA, K., AND HORI, H., *Bull. Chem. Soc. Jap.* **44**, 3216 (1971).
2. OZAKI, A., AIKA, K., AND MORIKAWA, Y., *Proc. Int. Congr. Catal., 5th,* Palm Beach, Pap. No. 90 (1972).
3. AIKA, K., HORI, H., AND OZAKI, A., *J. Catal.* **27**, 424 (1972).
4. PIETSCH, E. (Ed.), "Gmelins Handbuch der Anorganischen Chemie" System No. 21 (1966) and No. 22 (1953), Verlag Chemie, GMBH., Weinheim, Bergstrasse.
5. URABE, K., AIKA, K., AND OZAKI, A., *J. Catal.* **32**, 108 (1974).